Mixed order parameters, accidental nodes and broken time reversal symmetry in organic superconductors: a group theoretical analysis

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We present a group theoretic analysis of several classes of organic superconductors. We argue that highly frustrated half-filled layered organic superconductors, such as κ-$(ET)_2Cu_2(CN)_3$ (where ET is BEDT-TTF) and β'-$[Pd(dmit)_2]_2X$, undergo two superconducting phase transitions, the first from the normal state to a d-wave superconductor and the second to a $d+id$ state. We show that the monoclinic distortion of κ-$(ET)_2Cu(NCS)_2$ means that the symmetry of its superconducting order parameter is different from that of orthorhombic κ-$(ET)_2Cu[N(CN)_2]Br$. We propose that quarter filled layered organic superconductors, e.g., θ-$(ET)_2I_3$, have $d_{xy}+s$ order parameters.

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One of the most basic questions that can be asked about any phase of matter is, what symmetries does it spontaneously break? For example, all superconductors break gauge symmetry but many also break additional symmetries [1, 2]. Organic charge transfer salts are an important class of superconductor because they are highly tunable and have a number of exotic properties [3, 4, 5, 6] such as a small superfluid stiffness [6, 7], a Mott transition [8], spin liquid states [9, 10, 11], a 'bad metal' [4], pseudogap like behaviours [12], and charge ordered states [13]. Many of these properties are analogous to the cuprates [14] and this has heightened interest in organic superconductors as model systems. Yet, in spite of the two decades of intense effort to understand these systems, many basic questions remain unanswered. Of particular importance is the, still controversial, question of what is the symmetry of the superconducting state [15, 16].

In this Letter we use the methods of group theory to analyse the symmetries of the superconducting states in these materials. We discuss the pairing symmetries of κ-$(ET)_2Cu[N(CN)_2]Br$ (henceforth κ-Br) and κ-$(ET)_2Cu[N(CN)_2]Cl$ (κ-Cl) which we argue are '$d_{x^2-y^2}$', and κ-$(ET)_2Cu(NCS)_2$ (κ-NCS) which we show has additional components of other 'd-wave' states and thus accidental nodes (i.e., nodes that are *not* required by symmetry). Extending these arguments allows us to show that highly frustrated materials such as κ-$(ET)_2Cu_2(CN)_3$ (κ-CN_3) and β'-$[Pd(dmit)_2]_2X$ (β'-dmit) [17] will undergo two superconducting transitions the first from a normal metal to a 'd-wave' and the second from a 'd-wave' superconductor to a '$d+id$' state which breaks time reversal symmetry (TRS). Similar reasoning implies that the quarter filled organic superconductors have '$d_{xy}+s$' order parameters.

Group theory provides a powerful tool for addressing the symmetries of superconducting states as it does not assume any particular microscopic mechanism or theory of superconductivity [1, 2]. Such approaches are vital for the organic superconductors where there are clear signs that BCS theory, and indeed weak coupling approaches in general, are not sufficient to explain the observed experimental results, particularly the small superfluid stiffness [6, 7]. Further, the properties of nodal quasiparticles, which are determined by the symmetry of the superconducting state, have proved crucial in both the superconducting and pseudogap states of the cuprates [18].

Models of superconductivity based on both electron-phonon coupling [15] and the Hubbard model on an anisotropic triangular lattice [4, 15] have been proposed for the half-filled layered organic superconductors ($\frac{1}{2}$LOS). Calculations based on these two microscopic models lead to different conclusions. For phononic mechanisms both isotropic, nodeless 's-wave' states belonging to the A_1 irreducible representation (irrep) of C_{2v} and '$d_{x^2-y^2}$' states belonging to B_2 with nodes in the gap along the lines $k_x=k_y$ and $k_x=-k_y$ have been predicted. Calculations based on the Hubbard model suggest a (B_2) '$d_{x^2-y^2}$' state [6, 15, 19].

Experimentally, the pairing symmetries of κ-Br, κ-Cl, and κ-NCS are unclear. All show signs of unconventional superconductivity: there are no Hebel-Schlicter peaks [12], the thermodynamic measurements performed to the lowest temperatures show a power law temperature dependence [20] and the disorder strongly suppresses the superconducting critical temperature [16, 21]. Triplet superconductivity can be ruled out [16] on the basis of measurements of the Knight shift [12] and upper critical field.

Orthorhombic $\frac{1}{2}$LOS. Both κ-Br and κ-Cl are $\frac{1}{2}$LOS with orthorhombic (D_{2h}) crystal structures. There are four even parity irreps of D_{2h} (see table I) all of which are one dimensional. Canonically, the highly conducting plane is the ac plane in both κ-Br and κ-Cl. Further, it is usual to define the x- and y-axes as lying along the directions of the largest inter-dimer hopping integrals, which lie along the diagonals of the ab plane so that $\hat{\mathbf{x}}=(\hat{\mathbf{b}}+\hat{\mathbf{c}})/2$ and $\hat{\mathbf{y}}=(\hat{\mathbf{b}}-\hat{\mathbf{c}})/2$.

$\frac{1}{2}$LOS crystals are extremely anisotropic: the inter-plane hoping integral is about three orders of magni-

Irrep	Required nodes	Example basis functions ($k_z \| b$)	States	Example basis functions ($k_z \| c$)	States
A_{1g}	none	$1_{\mathbf{k}}$, $A^2_{\mathbf{k}}$, $B^2_{\mathbf{k}}$, $C^2_{\mathbf{k}}$, $X_{\mathbf{k}}Y_{\mathbf{k}}$	s, d_{xy}	$1_{\mathbf{k}}$, $X_{\mathbf{k}}Y_{\mathbf{k}}$, $1_{\mathbf{k}} + X_{\mathbf{k}}Y_{\mathbf{k}}$	s, d_{xy}
B_{1g}	line	$A_{\mathbf{k}}B_{\mathbf{k}}$, $(X_{\mathbf{k}} + Y_{\mathbf{k}})Z_{\mathbf{k}}$	$d_{(x+y)z}$	$A_{\mathbf{k}}B_{\mathbf{k}}$, $X^2_{\mathbf{k}} - Y^2_{\mathbf{k}}$	$d_{x^2-y^2}$
B_{2g}	line	$A_{\mathbf{k}}C_{\mathbf{k}}$, $X^2_{\mathbf{k}} - Y^2_{\mathbf{k}}$	$d_{x^2-y^2}$	$A_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} + Y_{\mathbf{k}})Z_{\mathbf{k}}$	$d_{(x+y)z}$
B_{3g}	line	$B_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} - Y_{\mathbf{k}})Z_{\mathbf{k}}$	$d_{(x-y)z}$	$B_{\mathbf{k}}C_{\mathbf{k}}$, $(X_{\mathbf{k}} - Y_{\mathbf{k}})Z_{\mathbf{k}}$	$d_{(x-y)z}$

TABLE I: The symmetry required nodes of the even parity irreps of the point group D_{2h}, which represents the symmetry of the orthorhombic organic superconductors such as κ-Br, in which the highly conducting plane is the a-c plane, i.e., $k_z \| b$, and θ-I_3, in which the highly conducting plane is the a-b plane, i.e., $k_z \| c$. The functions $1_{\mathbf{k}}$, $X_{\mathbf{k}}$, $Y_{\mathbf{k}}$, $Z_{\mathbf{k}}$, $A_{\mathbf{k}}$, $B_{\mathbf{k}}$ and $C_{\mathbf{k}}$ may be any functions which transform, respectively, as 1, k_x, k_y, k_z, k_a, k_b and k_c under the operations of the group and satisfy translational symmetry.

tude smaller than that in-plane [3]. The superconducting properties are also extremely anisotropic [3]. Hence, superconductivity in which the order parameter transforms as either the B_{1g} or B_{3g} irreps are extremely unlikely [2]. Therefore, a '$d_{x^2-y^2}$' state transforming as the B_{2g} irrep of D_{2h} is most consistent with the experimental and theoretical evidence.

Monoclinic $\frac{1}{2}$LOS. The best studied $\frac{1}{2}$LOS with a monoclinic crystal structure is κ-NCS. This material has a C_{2h} point group and the highly conducting plane is the bc plane. Here, the x- and y-axes are usually taken to be along the diagonals of the bc-plane. The only non-identity irrep of C_{2h} that corresponds to singlet superconductivity is B_g (see table II). This has symmetry required nodes only along the c-axis.

However, a subset of the possible choices for the basis function of the B_g irrep lead to '$d_{x^2-y^2}$' superconductivity (i.e., states with nodes along $k_x^2 = k_y^2$), which we have just argued is the superconducting state realised in the orthorhombic $\frac{1}{2}$LOS. Further, the properties of κ-NCS are so similar to those of κ-Br that the differences between the two materials are often described as 'chemical pressure' [5]. Therefore, one expects that the superconducting states of the two materials are closely related. If the node is shifted away from the b-axis in the higher symmetry, orthorhombic, case (as sketched in Fig. 1) then there is a change in symmetry which is accompanied by a phase transition. There is no requirement for such as phase transition in the monoclinic case as both possible the order parameters shown in Fig. 1 transform as the B_g irrep of C_{2h}. Any finite contribution to the superconducting order parameter from basis functions which do not have nodes along b-axis will cause this node to move or, for a sufficiently large contribution, disappear. Thus, predictions or measurements which show that monoclinic $\frac{1}{2}$LOS have nodes anywhere except along the c-axis are not robust. Therefore one cannot reliably conclude that the 'd-wave' (B_g) state is '$d_{x^2-y^2}$'. If there is an accidental node then it will not lie along b-axis and it may have either a temperature dependence, a k_z dependence or both.

The above argument also shows that calculations based on the anisotropic triangular lattice (whose symmetry is represented by the group C_{2v}) excludes components of the gap in a manner that is not relevant to the monoclinic $\frac{1}{2}$LOS. Thus weak interactions excluded by these models will dramatically change the symmetry of the gap. Even neglecting such interactions, at sufficiently low temperatures at least small additional '$d_{(x-y)z}$' components to the order parameter should be expected. Exotic states with more nodes than are present in '$d_{x^2-y^2}$' states have been proposed [22]. Such nodes would almost certainly be lifted in both monoclinic and orthorhombic $\frac{1}{2}$LOS as they are far from robust.

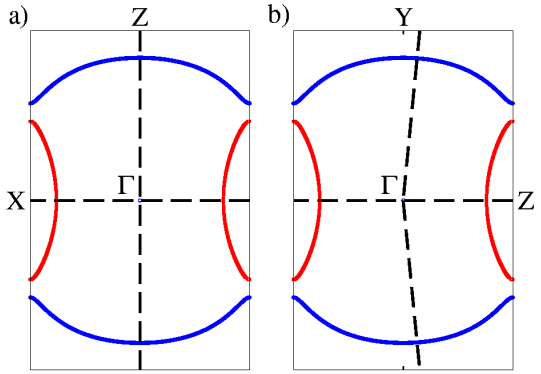

FIG. 1: (Color online.) Sketch of the differences between the nodal structures of (a) orthorhombic $\frac{1}{2}$LOS (e.g., κ-Br) and (b) monoclinic $\frac{1}{2}$LOS (e.g., κ-NCS). In both cases the Fermi surfaces are shown as solid lines and the nodes in the gap are shown as dashed lines. For $d_{x^2-y^2}$ states is orthorhombic $\frac{1}{2}$LOS symmetry requires that the nodes lie along the a- and c-axes. Whereas for d-wave states in monoclinic $\frac{1}{2}$LOS the only required symmetry is that the order parameter be antisymmetric under rotation by π about the z-axis. As a node is not required along the b-axis in the 'd-wave' state of the monoclinic $\frac{1}{2}$LOS we expect contributions from basis functions that do not go to zero along the b-axis to move this node and possibly remove this node altogether. High symmetry points are given their canonical labels.

TRS breaking in κ-CN_3 and β'-dmit. Much attention [11] has been focused on κ-CN_3 following the discovery that, in spite of there existing well formed local moments, in the low pressure, insulating phase, these moments do not order down to the lowest temperatures studied (20 mK) [9]. Both Huckel calculations [23] and fits of the susceptibility calculated by series expansions

Irrep	Required nodes	Example basis functions	States
A_g	none	$1_{\mathbf{k}}$, $A^2_{\mathbf{k}}$, $B^2_{\mathbf{k}}$, $C^2_{\mathbf{k}}$	s, d_{xy}
B_g	line	$\begin{cases} A_{\mathbf{k}}C_{\mathbf{k}}, (X_{\mathbf{k}}-Y_{\mathbf{k}})Z_{\mathbf{k}}, \\ B_{\mathbf{k}}C_{\mathbf{k}}, X^2_{\mathbf{k}}-Y^2_{\mathbf{k}} \end{cases}$	$\begin{cases} d_{x^2-y^2}, \\ d_{(x-y)z} \end{cases}$

TABLE II: The symmetry required nodes of the even-parity irreps of the group C_{2h} which represents the symmetry of κ-NCS and several other charge transfer salts with monoclinic unit cells. Note that the symmetry line node in the B_g irrep is required to lie in the plane $k_c = k_x - k_y = 0$.

[9, 24] to that observed experimentally suggest that the band structure of κ-CN_3 is that of the isotropic triangular lattice. Series expansions [10, 24] also show that the triangular lattice Heisenberg model is a good approximation for the low pressure, insulating phase of β'-dmit.

The symmetry of the triangular, or more correctly hexagonal, lattice is represented by the C_{6v} point group. An interesting feature of C_{6v} is that it has two two-dimensional (2D) irreps. In a 2D irrep the order parameter, $\Delta_{\mathbf{k}}$, is a linear combination of the basis functions, $\Psi^{1,2}_{\mathbf{k}}$, of the irrep, i.e., $\Delta_{\mathbf{k}} = \eta_1\Psi^1_{\mathbf{k}} + \eta_2\Psi^2_{\mathbf{k}}$. Hence, on the hexagonal lattice the Ginzburg-Landau free energy of order parameters belonging to the 2D irreps is [1, 2]

$$\begin{aligned} F_s - F_n &= \alpha(T-T_c)(|\eta_1|^2+|\eta_2|^2) + \beta_1(|\eta_1|^2+|\eta_2|^2)^2 \\ &\quad +\beta_2(\eta_1^*\eta_2 - \eta_1\eta_2^*)^2. \end{aligned} \tag{1}$$

The ground state solution, $\vec{\eta} = (\eta_1, \eta_2)$, is: (i) $\vec{\eta} = (1, 0)$ or (ii) $\vec{\eta} = (0, 1)$ for $\beta_2 > 0$ (the degeneracy is lifted by sixth order terms [1, 2]); (iii) $\vec{\eta} = (1, i)$ for $\beta_2 < 0$ (this is the weak coupling solution). In the E_2 irrep $\Psi^1_{\mathbf{k}}$ describes a '$d_{x^2-y^2}$' state and $\Psi^2_{\mathbf{k}}$ describes a 'd_{xy}' state. Thus the three solutions correspond to (i) '$d_{x^2-y^2}$' superconductivity; (ii) 'd_{xy}' superconductivity; and (iii) '$d_{x^2-y^2} + id_{xy}$' superconductivity. Thus state (i) is the same state as we have discussed above for the orthorhombic $\frac{1}{2}$LOS. However, a number of studies [25] of the Hubbard model on the hexagonal lattice suggest that state (iii) is realised.

The role of monoclinicity. It is important to realise that although the band structures of κ-CN_3 and β'-dmit are close to the hexagonal lattice, they will not be precisely that of the hexagonal lattice because these materials form monoclinic crystals. The monoclinic distortion of the crystal lowers the symmetry of the microscopic Hamiltonian. We account for this perturbation by introducing a symmetry breaking field, ε which, to lowest order, enters the free energy as $\varepsilon(|\eta_1|^2 - |\eta_2|^2)$ [26]. Thus,

$$\begin{aligned} F_s - F_n &= \alpha_+|\eta_1|^2 + \alpha_-|\eta_2|^2 + \beta_1(|\eta_1|^2+|\eta_2|^2)^2 \\ &\quad +\beta_2(\eta_1^*\eta_2 - \eta_1\eta_2^*)^2, \end{aligned} \tag{2}$$

where $\alpha_\pm = \alpha(T - T_{c\pm})$ and $T_{c\pm} = T_c \pm \varepsilon/\alpha$. This theory predicts that the monoclinic crystal will have two superconducting transitions, the first to either a '$d_{x^2-y^2}$' superconducting state or a 'd_{xy}' superconducting state (both of which have nodes) and the second to a, fully gapped, '$d_{x^2-y^2} + id_{xy}$' state. This leads us to propose the phase diagram sketched in Fig. 2. For small ε the difference in the two T_c's grows linearly with ε. But, for large ε the symmetry of the lattice will cease to be related to that of C_{6v} and return to that of C_{2v}. Therefore, for large ε all of the irreps are one-dimensional and, neglecting the possibility of accidental degeneracies, we expect a single superconducting transition. A similar scenario has previously been studied in some detail in the context of the double superconducting transition observed in UPt_3 [26]. However, for UPt_3 the proposed symmetry breaking field arises from a weak antiferromagnetic background [1], rather than from the crystal structure.

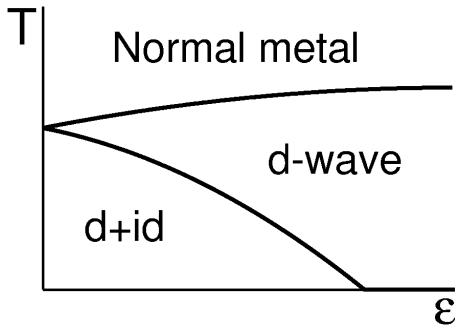

FIG. 2: Sketch of the proposed phase diagram for superconductivity near the hexagonal lattice in κ-CN_3 and β'-dmit. ε is a symmetry breaking parameter which lowers the symmetry from C_{6v} to C_{2h}. Physically ε could represent uniaxial strain or pressure. $\varepsilon \neq 0$ at ambient pressure due to the monoclinic crystal structure.

The above predictions are readily testable. Any number of experiments might see the double superconducting transition (e.g., specific heat or ultrasound). Further, the proposed low temperature '$d+id$' state breaks TRS, this could be detected directly by a number of experiments [1] most notably μSR [27]. Experimental confirmation of a double superconducting transition and broken TRS would be extremely important, not only because of the intrinsic interest in these phenomena, but also because they would be conclusive proof of unconventional superconductivity in the layered organic superconductors. The implication is then that phonons are not responsible for the superconductivity in these materials, but rather strong electronic correlations.

Quarter filled materials have been less studied experimentally, but, measurements of the in- and inter-plane penetration depths show power law dependencies suggesting unconventional superconductivity [28]. Some quarter filled layered organic superconductors ($\frac{1}{4}$LOS), e.g., θ-$(ET)_2I_3$ (θ-I_3), have unit cells with a D_{2h} point group, while others, e.g., β''-$(ET)_2SF_5CH_2CF_2SO_3$ (β''-SO_3), have C_i point groups. It has been proposed [13] that a minimal model for $\frac{1}{4}$LOS is the quarter filled extended Hubbard (or t-U-V-J') model on the square lattice. (Note that the unit cell used in this model is ro-

Point group	Example material	Irrep	State
C_{2h} (C_{6v})	κ-CN_3	$B_g + iA_g$ (E_2)	'$d + id$'
D_{2h}	κ-Br	B_{2g}	'$d_{x^2-y^2}$'
C_{2h}	κ-NCS	B_g	'$d_{x^2-y^2} + d$'
D_{2h}	θ-I_3	A_{1g}	'$d_{xy} + s$'
C_i	β''-SO_3	A_g	'$d_{xy} + s$'

TABLE III: Summary of the superconducting states proposed on the basis of the group theoretic analysis in this Letter. The parenthetic point group and irrep in the first row indicate the approximate symmetries which drive the physics.

tated with respect to the crystallographic unit cell so that $\hat{\mathbf{x}} = (\hat{\mathbf{a}}+\hat{\mathbf{b}})/2$ and $\hat{\mathbf{y}} = (\hat{\mathbf{a}}-\hat{\mathbf{b}})/2$.) This has led to the idea that charge and spin fluctuations may cooperatively mediate 'd_{xy}' superconductivity [13]. However, this prediction of the location of the nodes is not robust as the crystal lattices have significantly lower symmetries than the model. In the D_{2h} point group (table I) the basis functions that describe the 'd_{xy}' superconducting state belong to the trivial A_{1g} irrep. Therefore, these nodes are not robust in the same sense as '$d_{x^2-y^2}$' states are not robust in monoclinic $\frac{1}{2}$LOS . Thus one expects that the $\frac{1}{4}$LOS will have an '$d_{xy} + s$' order parameter. The order parameter may still have accidental nodes, but such nodes will be shifted away from the lines $k_x k_y = 0$. The same arguments and conclusions hold for $\frac{1}{4}$LOS with C_i point groups. A similar argument suggested that cuprates with a small orthorhombic distortion are '$s + d_{x^2-y^2}$' superconductors [29]. Tunnelling experiments have shown that the order parameter of YBCO does indeed have a significant s-wave component [30].

In summary, we have presented a group theoretic analysis of the several organic superconductors. This analysis has lead us to propose order parameters summarised in table III. In detail we have argued that orthorhombic $\frac{1}{2}$LOS (e.g., κ-Br and κ-Cl) have '$d_{x^2-y^2}$' order parameters but that monoclinic $\frac{1}{2}$LOS (e.g., κ-NCS) have nodes along the c-axis and possibly another node in the conducting plane that is *not* required by symmetry. We proposed that highly frustrated $\frac{1}{2}$LOS, such as κ-CN_3 and β'-dmit, have '$d_{x^2-y^2} + id_{xy}$' order parameters but the transition is split by the symmetry of the crystal so that there is first a transition from the normal state to a 'd-wave' superconductor and then a second phase transition from the 'd-wave' superconductor to a '$d + id$' superconductor. We argued that $\frac{1}{4}$LOS, e.g., θ-I_3, have '$d_{xy} + s$' order parameters.

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